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An Investigation of the Extraction of Deactivating Components from Synthetic Crudes with Supercritical Carbon Dioxide

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1.0 ABSTRACT

Four heavy oils, Suncor Coker Kerosene, Syncrude Coker Gas Oil, Syncrude Coker Naphtha and Suncor Coker Gas Oil were extracted with supercritical carbon dioxide in an attempt to remove sulphur and nitrogen containing compounds. In all fifty-nine extractions were carried out under a variety of temperatures and pressures. The use of certain co-solvents such as water, methanol and acetic acid was investigated. The extracted fractions were submitted to CANMET for micro analysis.

2.0. OBJECTIVE

Synthetic crudes derived from bitumen, heavy oils and residuals generally contain more nitrogeneous and sulphurous components than conventional oils and require considerably more processing. If these undesirable components could be removed less hydro-treating would be required to effect desulphurization and denitrogenation. Less catalyst would also be de-activated in these processes. To this end the extraction of heavy oils using supercritical carbon dioxide, with and without co-solvents, was studied to determine with selective extraction of sulphur and/or nitrogen containing fractions was possible.

3.0 PROPERTIES OF SUPERCRITICAL CARBON DIOXIDE

3.1. General

Carbon dioxide is a gas at all normal temperatures and pressures, but it can readily be condensed to solid or liquid. Solid carbon dioxide, popularly called "dry-ice", exists at a temperature of -80°C and is mainly used for mobile and temporary refrigeration, with minor quantities being used as a gas source. Solid carbon dioxide evaporates directly from solid to gas. Liquid carbon dioxide does not exist at normal atmospheric pressure, though it does at elevated pressures and at temperatures below 31.05°C, its critical temperature. Above the critical temperature and pressure, the compound only exists as a supercritical gas, sometimes called a supercritical fluid. At supercritical conditions the gas has many of the properties of both a gas and a liquid. (1)

The triple point, where gas, liquid and solid exist together in equilibrium, is at -56.69°C (216.56 °K) and 0.52 MPa pressure. Most of the investigations of the solvent power of carbon dioxide have been done at temperatures reasonably close to the critical temperature (31.05°C, 304.20°K), where the corresponding pressure is 7.4 MPa. At this point the densities of both the gas and the liquid are the same, that is 0.468g/ml (468kg/m^3). Figure 1 shows the relationship between the physical state of carbon dioxide and the temperature and pressure conditions in the system. (1)

3.1 General (cont'd)

The diagram clearly shows the boundary of the three phases, and their relationship to pressure. The nearer the system is to critical conditions the less the energy change required to change the phase state. At the critical point itself no energy is required to vapourise liquid carbon dioxide.

In the same way there are considerable changes in liquid density as critical conditions are approached, the density halving between -18°C and 31°C. These changes are illustrated in Figure 2.

Above the critical point density is a function of both temperature and pressure. Higher pressures increase density, higher temperatures decrease it. In these circumstances the normal gas laws are not strictly obeyed, the gas laws applying best when the gas is at conditions far from its critical point.

Density is an important factor in determining the solubility of various products, thus solubility can be controlled by temperature and pressure above 31°C and mainly by temperatures below that temperature. When a liquid phase is present the system will tend to move towards equilibrium conditions which will govern the actual pressure.

3.1 General (cont'd)

Both as a liquid and a supercritical gas, carbon dioxide acts as a non-polar (non-ionising) solvent, in many ways like hexane. Usually the solubility of a solute will increase with an increase in density; below critical conditions, density increases rapidly with lowering temperature and above these conditions it rises with increasing pressure and falls with increasing temperature. Under supercritical conditions the dielectric constant also increases with increasing pressure, this being a measure of the solvent (polar/non-polar) characteristics of the carbon dioxide. Hydrocarbons dissolve most readily in non-polar (low dielectric constant) solvents. By controlling both temperature and pressure the character and solvent power of supercritical carbon dioxide can be "fine-tuned".

Most compounds increase in solubility with increasing temperature, however they also become less soluble with decreasing density. Many compounds have a maximum solubility in liquid carbon dioxide, often at around 5° to 10°C. Above critical conditions solubility of most non-polar compounds increases with pressure. Under supercritical conditions some compounds increase in solubility as the temperature rises at higher pressures but decrease in solubility at lower but still supercritical pressures.

Figure 1

The Physical States of Carbon Dioxide

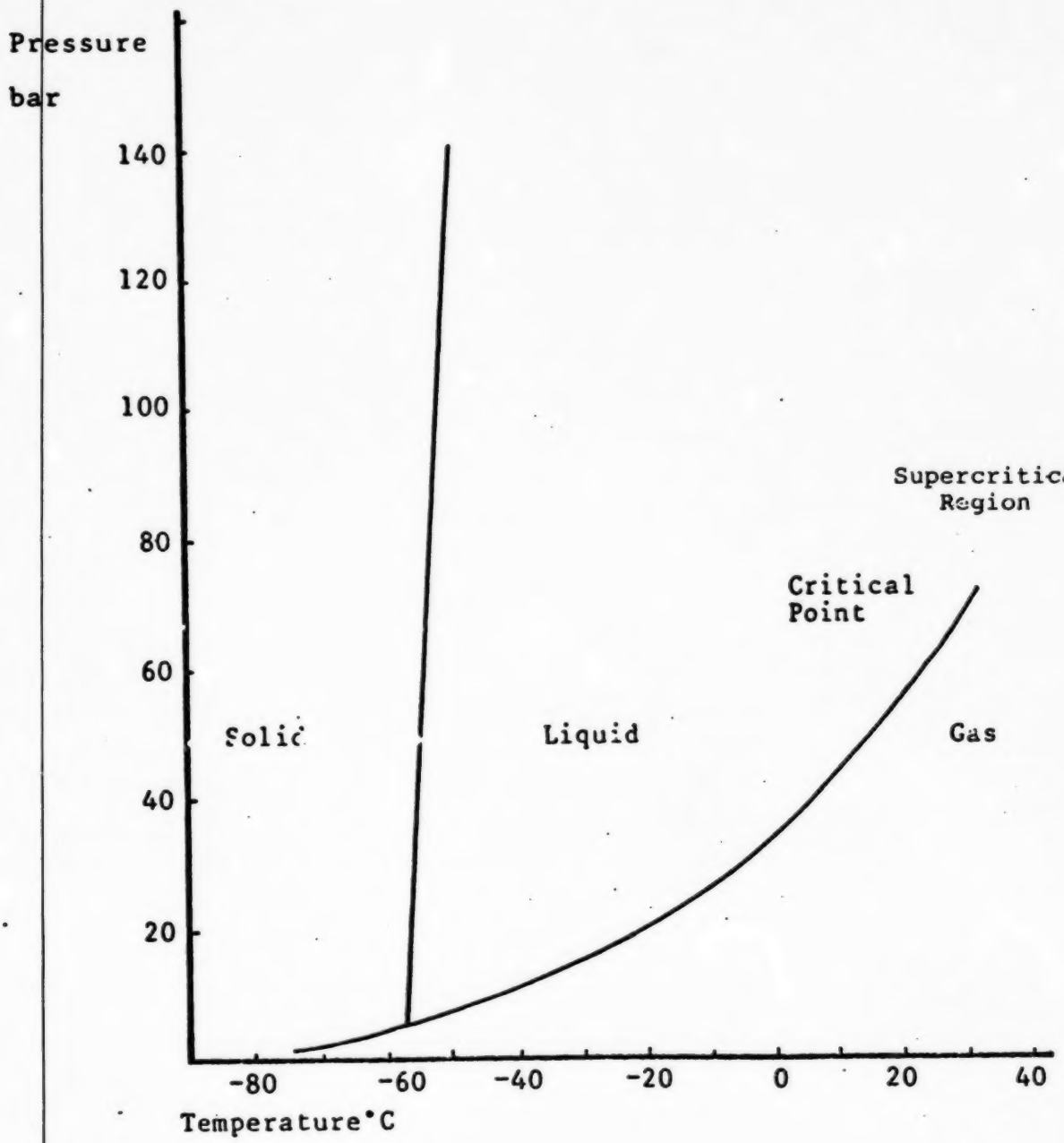
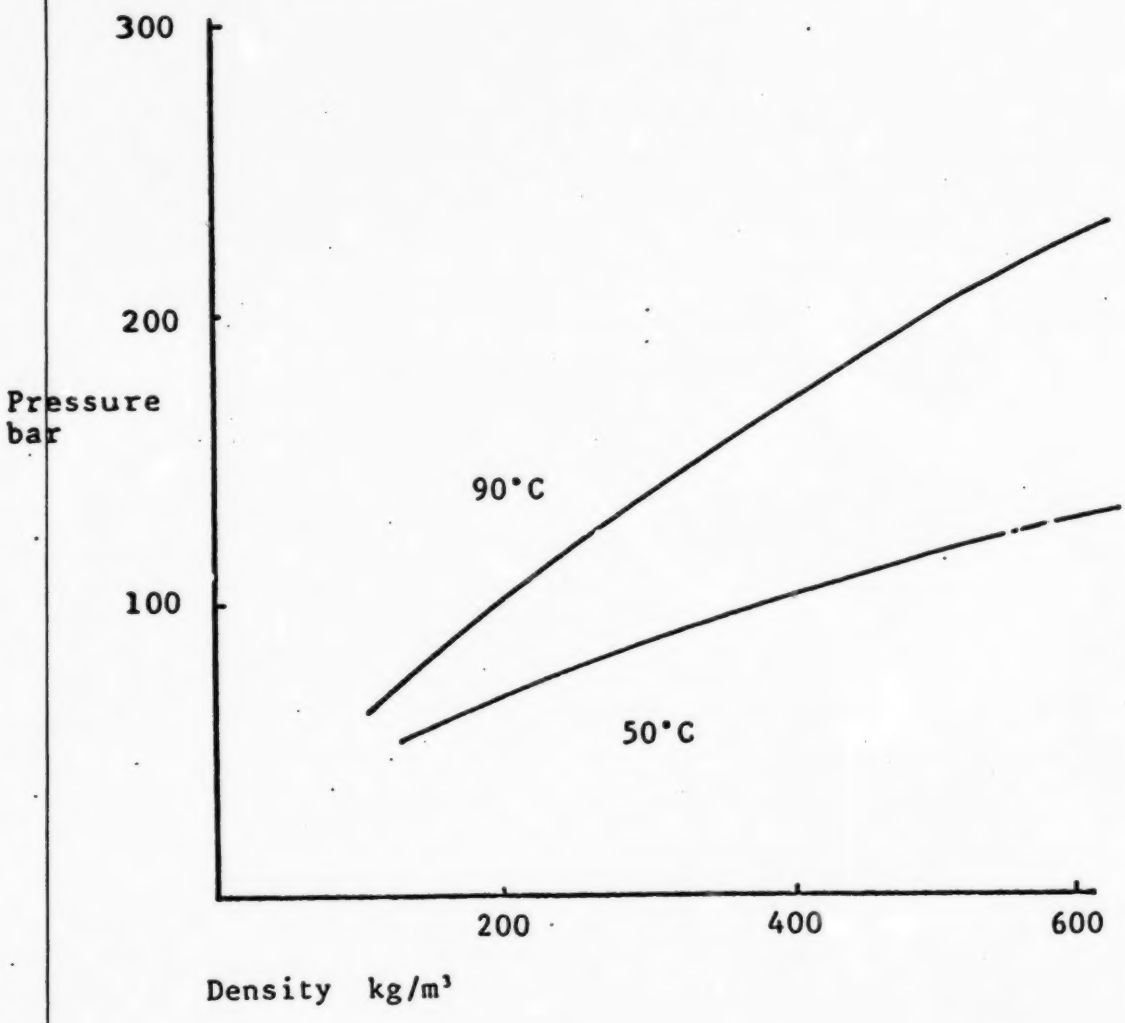


Figure 2

Density of Supercritical Carbon Dioxide



3.1.1 SOLUBILITY OF COMPOUNDS IN CARBON DIOXIDE

There are a number of general rules governing the solubility of compounds in carbon dioxide. The more non-polar a compound is, the more likely it is to dissolve in either liquid or supercritical carbon dioxide. Most hydrocarbons and essential oils are soluble. Alkaloids are soluble at higher pressure under supercritical conditions.

Polar functions such as hydroxyl, carboxyl, or nitrogenous groups etc... tend to lower solubility. Polar compounds are only soluble if they are of low molecular weight. Sugars, amino acids, fatty acids and most inorganic compounds are insoluble. Fatty acid esters are more soluble than the fatty acids and their glycerols. Although it seems a contradiction, many polar low molecular weight organic solvents which are miscible in water such as ethanol, are also miscible with supercritical carbon dioxide under certain conditions.

3.2. OTHER GASES

Carbon dioxide is not the only gas that can be handled as a supercritical fluid with solvent power. As a simple rule, if the gas has been used as the basis of a refrigerant cycle, however tenuously, it may be used as a supercritical solvent, at readily obtainable pressures and near normal temperatures.

3.2. OTHER GASES (cont'd)

The list of gases includes ammonia, sulphur dioxide, nitrous oxide, ethylene, and the fluorochlorocarbon refrigerants such as R12. Other compounds may be used as supercritical solvents under more rigorous conditions of higher pressures or temperatures include organic liquid solvents, e.g. ether and permanent gases such as nitrogen. (1) Physical data for some gases usable for extraction are given in Table A.(2)

TABLE A

PHYSICAL DATA FOR SOME GASES USABLE FOR EXTRACTION

GAS	B.p.(°C) at 1 bar	Tc (°C)	Pc (Bar)	Dc (g/ml)	Dielectric constant at 1 bar 0°(e)
Carbon dioxide	-78(Subl)	31.3	73	0.448	1.0011
Nitrous oxide	-89	36.5	71	0.457	1.00113
Ammonia	-33.4	132.3	111	0.24	1.0072
Ethylene	-103.7	9.5	50	0.20	1.0018
Ethane	-88	32.4	48	0.201	1.0015
Propane	-44.5	96.8	42	0.220	--

3.3 HISTORY OF EXTRACTIONS WITH SUPERCRITICAL CARBON DIOXIDE (3)

The technology for extraction with supercritical fluids begins in 1879 when Hannay and Hogarth (4) studied the solubility of inorganic salts in ethanol and ether. In the period between 1900 and 1950, various researchers studied the solubilities of organic compounds. From 1955 until the present there have been studies of the solubility and its application to extraction procedures. Beginning in 1970 the first commercially feasible industrial applications appeared. Zhuse (5) in 1955 utilized supercritical propane/propylene mixtures, which are much superior to liquid propane for the purification of distillation residues of vapour cracking. More recently Just and Schachner (6) made a preliminary investigation on the extraction of organic material from Athabasca tar sands using supercritical carbon dioxide in a closed system operating between 22-150°C and 900 3900 psig. They determined that two maxima occurred: one at 37°C and 1050 psi when 43% of the organic material was extracted. A second maximum at 120-125°C and 3100-3900 psi resulted in the extraction of a further 49% organic material. Much study has also been devoted to the extraction of coal using such supercritical fluids as toluene (7) and water (8). Finally this extraction technique has been employed in a number of other processes including gas chromatography and the extraction of paraffin from mineral ores (9).

4.0 NATURE OF NITROGENOUS AND SULPHUROUS COMPONENTS OF SYNTHETIC CRUDES

Nitrogenous bases in petroleum and related crudes belong to the classes of azarenes (nitrogenated polyaromatic hydrocarbons, NPAH) and of primary aromatic amines. The concentration of these compounds in crude is usually low, less than 100 ppm being a typical concentration for an azarene fraction in virgin crude oils. In synthetic crudes this level is frequently exceeded. In general these compounds are (with the exception of a few primary aromatic amines) non-polar; their properties can vary from moderately strong bases, (and moderately polar) such as analine and its alkylated analogues, to virtually neutral or very weak bases such as phenazine (non-polar) quinoline (weakly polar) or acridine (weakly polar) and their benzo-homologues and to the weakly acidic homologues of pyrrole such as indole or carbazole.

Sulphur containing molecules are also primarily weakly polar polynuclear heteroaromatics related to thiophene. Typically benzothiophene and dibenzothiophene are important constituents of this fraction. Lower in concentration and usually present in only trace quantities are the more polar aromatic and aliphatic thiols, sulphides and di- and polysulphides. Oxidised derivatives such as sulphoxide and sulphones are also frequently present, albeit in trace amounts. Both nitrogen and sulphur hetero-

4.0 NATURE OF NITROGENOUS AND SULPHUROUS COMPONENTS OF SYNTHETIC CRUDES (cont'd)

cycles are generally only slightly more polar than their carbocyclic analogues. The solubility of these classes of compounds do not display any large differences from carbocyclic systems. This is particularly true in those cases where a single heteroatom is present in a multiring molecule.

5.0 EXTRACTION TEMPERATURES AND PRESSURES

Since the dielectric constant increases with increasing pressure the ability of supercritical CO_2 and N_2O to dissolve polar organic molecules will increase as the pressure is increased. At 50°C a relatively small change in pressure results in a very large change in density (and also in dielectric constant). In order to investigate the effect of pressure on the solubility of the nitrogen and sulphur containing molecules it is therefore desirable to work at temperatures close to the critical point, where small changes in the pressure should result in relatively large changes in the solubility characteristics. (10-14)

Stahl (2) noted that the dielectric constant of CO_2 increases rapidly up to 200 bars (3000 psi.) to a value of approximately 1.5 and then slowly increases to 1.6 at 600 bar (8700 psi). In general there appears to be a consensus that hydrocarbon and other typically lipophilic organic compounds of low polarity (15) such as esters, ethers and lactones can be extracted in the low pressure region between 70 and 100 bar (1015 and 1450 psi) and at relatively low temperatures (40°C). Best fractionation of hydrocarbons was also found to occur between 70 and 100 bar (1015 and 1450 psi). (2)

Based on these considerations we recommended the extraction conditions set out in Table B as an appropriate set of initial experiments.

TABLE B

RECOMMENDED EXTRACTION CONDITIONS: CO_2
CRITICAL TEMPERATURE: 31.05°C;
CRITICAL PRESSURE 1070 psi.

RUN NO.	TEMPERATURE °C	PRESSURE, psi.
1	40	1100
2	40	1300
3	40	2500
4	45	1100
5	45	1300
6	45	2500
7	50	1100
8	50	1300
9	50	2500
10	60	1100
11	60	1300
12	60	2500

The density of CO_2 at 2500 psi (172 bars) is 0.8 g/ml; an increase to 5000 psi (344 bar) provides only a small increase in density to approximately 1.0 g/ml. The dielectric constant also changes only modestly from e = 1.45 to 1.63 for the same large increase in pressure. Pressures in excess of 2500 psi therefore yield diminishing returns in terms of their ability to enhance the solubilizing power.

By small increases in temperature small reductions in density and dielectric constant of the solvent are effected. We believed that most non-polar nitrogen and sulphur heterocycles would be extracted under the conditions of runs 10, 7, 4 and 1 while more polar compounds would be extracted under conditions of runs 12, 9, 6 and 3. Runs 11, 8, 5 and 2 would provide intermediate conditions. However, it was recognized that the solubility characteristics are not always predictable, since the solubility of some compounds will increase as the temperature rises despite the decrease in dielectric constant. Higher extraction temperatures could be substituted if greater selectivity were required to extract the sulphur and nitrogen containing non-polar fractions. The conditions selected permitted 'fine tuning' at the low dielectric end where most of the sulphur and nitrogen heterocycles were expected to be extracted.

6.0 EXTRACTION USING SUPERCRITICAL NITROUS OXIDE

The behavior of N_2O as a supercritical solvent was not expected to differ markedly from that of CO_2. Relatively few references pertain to the use of N_2O. Stahl (2,16-19) has investigated the use of this gas for extraction of alkaloids at 40°C and 70-400 bar; more polar materials such as resin acids can be extracted from Douglas and Pinewood fir barks at 40°C and 20-60 MPa. Supercritical extraction of petroleum oils with N_2O and with mixed solvents has been investigated (10,12) as has its dissolving capacity for naphthalene, naphtol and other hydrocarbons. Extractions were similar to those obtained from petroleum ether (13).

7.0 EXPERIMENTAL

7.1 REACTOR DESIGN

A supercritical gas extractor was constructed as depicted in Figure 3. The system was based on 1 liter agitated reactor unit (Pressure Product Industries Serial No. AOH-34537) equipped with a permanent magnet drive. The vessel was constructed of 316 stainless steel and was rated at 5000 psi w.p. at 650°F (343°C). Agitation was achieved with a flat multiblade turbine set screwed to a one piece shaft. The permanent magnetic drive was mounted on the cover of the vessel and was driven by means of a V-belt at approximately 500 rpm.

The extractor gas was pumped with a Model LS30 Pulsafeeder diaphragm metering pump (Pulsafeeder Products) rated at 3000 psi w.p., and having delivery capacity of 0.15 gph. The collector vessel had a 50 ml. capacity and was constructed with 304 stainless steel; the vessel was rated at 3400 psi w.p. The temperature of the interior was recorded by means of a moveable thermocouple and was displayed on a Digimite digital thermometer. Overpressure protection was provided by a rupture disc (Autoclave Engineering), with a pressure limit of 3000 psi at 72°F (22°C). All tubing was stainless steel. For further details see Appendix 1 "List of Components".

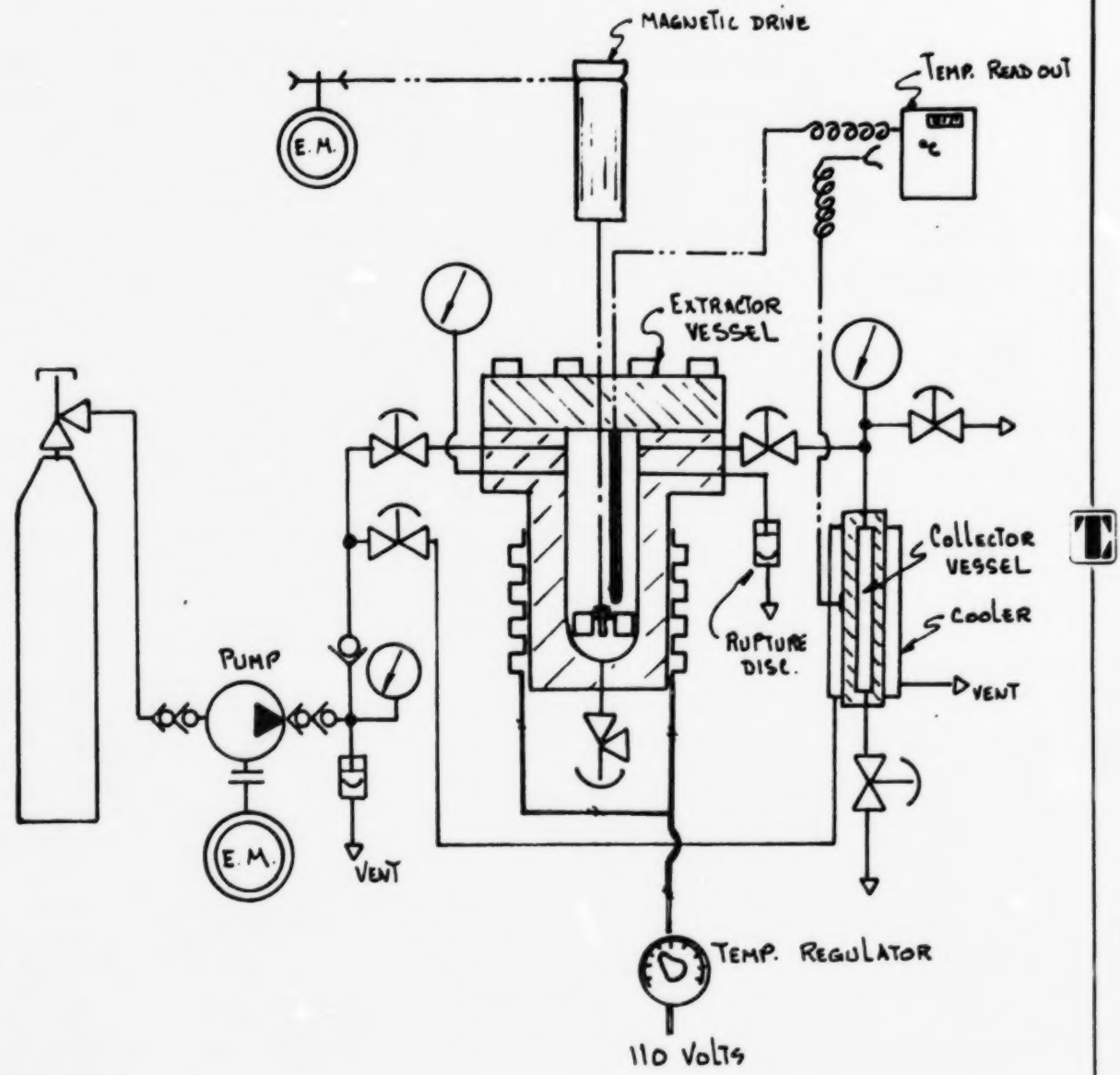


FIGURE 3

SUPERCRITICAL GAS EXTRACTION
FLOW DIAGRAM

The unit was tested to a pressure of 2800 psig using liquid kerosene as a probe for leaks occurring between the pump and the collector valve for the let-down vessel. This check also served to verify the operation of the Pulsafeeder pump at pressures required.

Carbon dioxide (Matheson) or nitrous oxide (Matheson) was used as supplied without any purification.

Four heavy oils (Suncor Coker Kerosene 8216, Syncrude Coker Gas Oil 8421, Syncrude Coker Naphtha 8335 and Suncor Coker Gas Oil 8210) supplied by CANMET were extracted with supercritical carbon dioxide alone and with co-solvents under different conditions of temperature and pressure. In all 59 runs were carried out.

7.2. REACTOR OPERATION

Initial tests showed some difficulty in controlling temperature and pressure. It was found that pumping carbon dioxide in a mixed liquid/supercritical gas state was difficult in that the gas tends to cavitate in the pump. The problem was largely overcome by permitting liquid CO_2 to flow through the pump during the initial filling process. The expansion of gas cooled the pump and associated plumbing to -45°C. At this temperature the CO_2 was kept in the liquid phase for sufficient time to establish the required pressures. The most reliable technique was to charge the system with liquid CO_2

to a predetermined pressure at approximately -40°C (in the extraction vessel) and on warming the desired pressure and temperature was reached. The runs were standardised on the basis of 200 ml of oil to be extracted and a 3-3.5h extraction time. Typically the following procedure was adopted.

The oil (200 g) was introduced into the one litre reactor. The venting valve between the extraction inlet valve and the check valve was closed. The extraction vessel outlet valve was left open and the sample collector valve at the base of the collector vessel was closed. The vent valve between the extractor outlet valve and the collector vessel was initially left slightly open permitting the extraction gas to pass into the atmosphere. The gas cylinder was then cautiously opened permitting the gas to exhaust through the Pulsafeeder pump, the extraction vessel and through the open vent valve for approximately 4-5 minutes. During this period all lines were cooled to ca. -40°C at which point liquid CO_2 was seen to escape through the collector vent valve. By judicious manipulation of the vent and the cylinder outlet valves the pressure was permitted to slowly increase to 200 psig. The outlet valve to the extraction vessel was then rapidly closed and the Pulsafeeder pump and temperature regulator turned on. The temperature was permitted to rise to ca. 6°C during the compression phase. (The description which follows applies to a run carried out at 1200 psig.). When the extraction vessel pressure gauge indicated 800 psig the pump was shut off and the extractor inlet and cylinder outlet valves were closed.

The temperature of the extraction vessel was then carefully increased to 40°C at which point the indicated pressure rose to 1200 psig. (If the pressure increased above the desired (1200 psig) level it could be adjusted by slowly opening the outlet valve between the extractor and collector vessels). When steady state conditions had been achieved (after approximately 30 minutes) the magnetic stirrer drive was turned on and the recording of pressure and temperature commenced, the latter being adjusted by means of the temperature regulator. The total extraction time was generally 210 minutes.

7.3. SAMPLE COLLECTION

The stirrer and temperature regulator were turned off at the end of the run and the vent valve at the head of the collection vessel was closed. The extraction vessel outlet valve was cautiously opened and the product under pressure was directed to the collector vessel. When pressurization of the collector vessel was complete, both pressure gauges (extractor and collector) registered 1000 psig. The sample collector valve was then slowly opened and sample dissolved in the carbon dioxide was collected. When the pressure dropped to 800 psig the remaining CO_2 was vented as a gas.

7.4. FRACTIONS COLLECTED AND THEIR IDENTIFICATION

Typically the first fraction (01) was collected after 3.5h extraction time. At the end of this period a second fraction (02) was obtained from supernatant carbon dioxide which had accumulated in the collection arm between the extractor and collector vessels. In order to obtain this sample the collection arm was cooled to liquify the carbon dioxide and then slowly decompressed. A third sample ("decompression volume/weight") was obtained from material that blew out as the pressure in the extractor vessel was slowly increased. The sample was assumed to be similar in composition to fraction 02 but may also have contained oil which bubbled or spattered over as decompression took place. No record was kept of the decompression sample until run No. 19 (data was also absent for some runs after No. 19). A final sample ("residue") was collected after decompression and comprised the residual oil drained from the bottom of the extraction vessel.

7.5 COSOLVENTS

Three cosolvent systems were investigated: Acetic acid (4g) was added to Suncor Coker Gas Oil 8218 (200g) or Suncor Coker Naphtha (200g) and the resulting mixture was extracted with supercritical CO_2 under different conditions of temperature and pressure. Similarly Suncor Coker Naphtha 8217 (200g) was mixed with either water (4g) or with methanol (4g) as cosolvent, the system subsequently being extracted with supercritical CO_2 under different conditions of temperature and pressure.

7.6 SAMPLE CODING

Samples submitted to CANMET for microanalysis (C,H,N,S) were identified using a fourteen digit code, the first two digits of which were the run number followed by four digits identifying the oil followed by six digits giving the date of the experiment (Year, Month, Day). The final two digits identified the fraction collected.

7.7 SUMMARY OF RESULTS

Table 1: SYNCRUDE COKER NAPHTHA 8335 EXTRACTION DATA
(CARBON DIOXIDE: NO COSOLVENT)

Run No.	Run Time (h)	Pressure (psig)	Temperature (C)	Fraction Extract Weight(g) 01	02	Decompression Volume (ml)	Residue Volume (ml)
01[a]	3.5	1200	40	15.0	10.0	-	-
15	3.5	1500	90	53.3	-	-	-
16	3.25	2800	90	36.3	8.6	-	-
17	3.17	2600	60	17.2	10.8	-	-
21	3.5	2550	60	21.6	9.17	30	110
22	3.5	2050	60	19.5	10.0	35	110
23	3.5	1775	60	17.2	7.0	50	100
24	3.5	1550	60	6.8	2.8	70	100
25	3.5	2500	75	20.0	11.0	70	95
26	3.5	2000	75	18.9	10.1	60	90
27	3.5	1750	75	7.9	1.9	70	95
28	3.5	1525	75	5.5	0.8	80	95
29	3.5	1550	90	5.1	0.7	50	95
30	3.5	2500	90	20.0	8.0	30	110
31	3.5	2050	90	10.8	4.1	66	87
32	3.5	1750	90	7.0	1.5	80	95
33[b]	3.5	2300	60	26.5	4.8	30	180

(a) No cooling system on collector vessel on Run No. 1.

(b) The weight of Coker Naphtha extracted was 200g in all cases except for Run No. 33 where 300 ml was employed.

TABLE 2: SYNCRUDE COKER GAS OIL 8421 EXTRACTION DATA (CARBON DIOXIDE: NO COSOLVENT)(d)

Run No.	Run Time (h)	Pressure (psig)	Temperature (C)	Fraction Extract Weight 01	02	Decompression Volume (ml)	Residue Volume (ml)
02(a)	4.0	1200	40	0.0	0.0	(c)	(c)
09	3.0	1850	60	1.5(b)	0.0	(c)	(c)
10	4.0	2350	45	7.1(b)	0.0	(c)	(c)
11	3.15	2000	45	3.3(b)	0.0	(c)	(c)

(a) After run No. 6 a cooling system was installed around the collector vessel.

(b) Weights reported represent the combined weights of extracts 01 and 02.

(c) "Decompression Volume" collected and "residue volume" were not measured for these runs.

(d) Weight of Coker Gas Oil extracted: 200g in all cases.

TABLE 3: SUNCOR COKER KEROSENE 8216 EXTRACTION DATA (CARBON DIOXIDE: NO CO-SOLVENT)[a]

Run No.	Run Time (h)	Pressure (psig)	Temperature (C)	Fraction Extract Weight(g) 01	02	Decompression Volume(ml)	Residue Volume (ml)
04[b]	4.0	1200	40	10.3	1.8	(c)	(c)
18	3.0	2400	45	25.2	6.6	(c)	75
19	3.16	2550	60	18	6.9	50	125
20	3.16	2000	90	4.4	0.5	(c)	(c)

(a) Weight of Coker Kerosene extracted: 200 g in all cases.

(b) No cooling system on collector vessel prior to run No. 6.

(c) No data recorded.

TABLE 4: SUNCOR COKER GAS OIL 8218 EXTRACTION DATA (CARBON DIOXIDE: NO CO-SOLVENT)(a)

Run No.	Run Time (h)	Pressure (psig)	Temperature (C)	Fraction Extract Weight(g) 01	02	Decompression Volume(ml)	Residue Volume (ml)
05(b)	4.0	1200	45	0.6	(c)	(c)	(c)
06(b)	2.0	1200	45	0.0	0.0	(c)	(c)
07	3.8	1650	45	0.6	0.0	(c)	(c)
08	3.75	2000	60	3.9	0.0	(c)	(c)
34	3.5	1175	60	0.0	0.0	0.0	195
35	3.5	2050	60	2.6	1.3	0.0	195
36	3.5	1750	60	1.5	0.5	0.0	195
37	3.5	2550	90	1.2	2.1	0.0	175

(a) Volume of Gas Oil extracted: 200 ml in all cases.

(b) No cooling system on collector vessel.

(c) No data recorded.

(d) Weights recorded represent the combined weights of extracts 01 and 02.

TABLE 5: SUNCOR COKER NAPHTHA 8217 EXTRACTION DATA
(CARBON DIOXIDE: NO CO-SOLVENT)[a]

Run No.	Run Time (h)	Pressure (psig)	Temperature (C)	Fraction Extract Weight(g) 01	02	Decompression Volume(ml)	Residue Volume (ml)
03[b]	4.0	1200	40	0.0	0.0	(c)	(c)
12	3.0	2400	45	39.6	0.0	(c)	(c)
13	3.0	2100	45	22.3	0.0	(c)	(c)
14	3.5	1200	60	20.2	0.0	(c)	(c)
38	3.5	1250	90	2.4	0.0	0.0	175
39	3.5	2050	90	9.0	3.2	78	80
40	3.5	2550	90	17.5	7.2	60	90
41	3.5	1800	90	6.3	2.5	80	(c)
42[d]	3.5	2500	65	0.0	7.26	(c)	100

(a) Weight of Coker Naphtha Extracted: 200 g in all cases.

(b) No cooling system on collector vessel.

(c) No data recorded.

(d) Leak developed in seal of extraction vessel during this run.

TABLE 6: SYNCRUDE COKER NAPHTHA 8335 EXTRACTION DATA (CARBON DIOXIDE WITH WATER AS CO-SOLVENT)(a)

Run No.	Run Time (h)	Pressure (psig)	Temperature (C)	Fraction Extract Weight(g) 01	02	Decompression Weight(g)(b)	Residue Volume (ml)
43	3.5	1200	40/43	15.0	1.2	21.2	165
44	3.5	2025	40	23.2	6.2	13.8	175
45	3.5	1300	90	3.0	0.4	37.3	145
46	3.5	2050	90	12.2	5.6	117	122

(a) Weight of Coker Naphtha extracted: 200 g in all cases.

(b) Note: Unlike Tables 1-5, the fraction collected during decompression is recorded in kms. of weight.

TABLE 7: SYNCRUDE COKER NAPHTHA 8335 EXTRACTION DATA (CARBON DIOXIDE WITH ACETIC ACID AS CO-SOLVENT)(a)

Run No.	Run Time (h)	Pressure (psig)	Temperature (C)	Fraction Extract Weight(g) 01	02	Decompression Weight(g)(b)	Residue Volume (ml)
47	3.5	2000	40	19.1	4.2	10.9	192
48	3.5	1200	40	19.8	1.2	24.0	117
49	3.5	2050	90	11.4	3.7	75.5	115
50	3.5	1300	90	3.4	1.6	35.6	180
51	3.5	2050	90	13.7	6.3	38.3	155

(a) Weight of Coker Naphtha extracted: 200 g in all cases.

(b) Note: Unlike Tables 1-5, 9 the fraction collected during decompression is recorded in terms of weight.

TABLE 8: SYNCRUDE COKER NAPHTHA 8335 EXTRACTION DATA (CARBON DIOXIDE WITH METHANOL AS CO-SOLVENT)(a)

Run No.	Run Time (h)	Pressure (psig)	Temperature (C)	Fraction Extract Weight(g) 01	02	Decompression Weight(g)(b)	Residue Volume (ml)
52	3.5	1350	40	24.5	1.5	15.2	190
53	3.5	2000	41.5	24.2	7.6	8.0	180
54	3.5	2050	90	11.1	4.8	66.3	120
55	3.5	1350	90	4.2	1.1	59.5	145

(a) Weight of Coker Naphtha extracted: 200 g in all cases.

(b) Note: Unlike Tables 1-5,9 the fraction collected during decompression is recorded in terms of weight.

TABLE 9: SUNCOR COKER GAS OIL 8218 EXTRACTION DATA
(CARBON DIOXIDE WITH ACETIC ACID AS CO-SOLVENT)(a)

Run No.	Run Time (h)	Pressure (psig)	Temperature (C)	Fraction Extract Weight(g) 01	02	Decompression Volume(ml)	Residue Volume (ml)
56	3.0	1300	40	3.2	36.7	0.0	150
57	3.0	1300	90	1.4	0.8	0.0	210
58	3.0	2050	40	2.7	29.2	0.0	120
59	3.0	2100	90	3.4	0.65	4.0	200

(a) Weight of Coker Gas Oil extracted: 200 g in all cases.

8.0 DISCUSSION

Samples from each of the 59 runs were submitted to CANMET for microanalysis. Although TECHNITROL did not obtain details of the results, it appears that there occurred little or no concentration of sulphur or nitrogen containing moieties in the supercritical gas extracts. Thus, although some fractionation of the heavy gas oil is possible, the dielectric constants of the sulphurous and nitrogeneous compounds evidently closely resemble those of the hydrocarbons present making selective extraction impossible. No improvement in selectivity was observed when co-solvents such as water, methanol or acetic acid were present.

9.0 CONCLUSION

Supercritical carbon dioxide was unsuccessful as a solvent for the selective removal of sulphur and nitrogen containing compounds encountered in four heavy gas oils submitted to TECHNITROL by CANMET.

* * * * * *

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APPENDIX I

APPENDIX I

LIST OF COMPONENTS
SUPERCRITICAL EXTRACTION SYSTEM

Qty	Description	Manufacturer
1	AOH-34537 One Liter Agitated Reactor Unit with Permanent Magnetic Drive - 316 Stainless Steel - 5000 PSI W.P.at 650°F.	Pressure Products Industries
1	Model LS30 Pulsafeeder Diaphragm Metering Pump 3000 PSI, MAX.W.P. .15 GPH Capacity	Pulsafeeder Products
1	50 ml. Capacity, Collector Vessel 304 Stainless Steel, 3/4" O.D. .065 wall thickness, 3400 PSI W.P.	Technitrol
1	Digimite Digital Temperature Indicator	Digimite
2	Model 233-50 4" Pressure Gauge 0.5000 PSI - Stainless Steel Tube & Socket	Wika
2	SS .645 FP 111GP Pressure Stainless Steel Valve	SNE TRIK
2	SC4081-TG Stainless Steel Valve	Autoclave Engineers
1	SS.3NBF4. Stainless Steel 1/4 NPT Valve	Whitey
1	CXO44 OD Stainless Steel Check Valve	Autoclave Engineers
1	HBT 45 120/240V 750 Watts Tubular Heater Band	Chromalox
1	MC 115V 1500 Watt Temperature Regulator	Electro-thermal
	3/8 O.D. Tubing, .065" Thick, 304 Stainless Steel	
	1/4 O.D. Tubing, 316 Stainless Steel Tubing	

PRESSURE PRODUCTS INDUSTRIES
DIVISION OF THE DURIRON COMPANY, INC.
900 Louis Drive • Warminster, Pennsylvania 18974 • 215 · 675 · 1600 • Telex 84 · 5329

DESIGN SPECIFICATIONS

Bulletin 310 3M5

MODEL 3M5 AGITATED REACTOR

SPECIFICATIONS

DESCRIPTION

Model Number - 3M5
Capacity - One Liter
Internal Dimensions - 3.0" ID x 9⅛" IL
Design Pressure - 5,000 PSIG
Design Temperature - 650° F
Hydrotest Pressure - 8,800 PSIG

MATERIALS OF CONSTRUCTION

Body - SA-182-F-316
Cover - SA-240-T316
Closure Seal - 316 SS/Asbestos
Cooling Coil - 316 SS (3/16" OD x 1/8" ID)
Sample Tube - 316 SS (3/16" OD x 0.090" ID)
Thermowell - 316 SS
Agitator - 316 SS
Closure Bolts - SA-19387

CLOSURE DESIGN

Fully confined spiral wound gasket compressed in a full flange.

PROCESS & SERVICE CONNECTIONS

Rupture Assembly - 1/4" Diameter, Body
Sample Tube - 1/4" Low Pressure, Cover
Process (4) - 1/4" Low Pressure, Body
Gas Purge - 1/4" High Pressure, Drive
Cooling Coil - 1/4" N.P.T., Cover
Thermowell - Cover
Drive Jacket - 1/4" N.P.T., Drive

HEATING

Electric mantle heater rated at 1.2 KW for 120 1/60 power supply. The mantle heater contains its own insulation.

AGITATOR DRIVE

Permanent Magnetic Drive (PMD) with carbon bearings and inner magnetic assembly canned in 316 SS. The drive transmits 0.25 horsepower at 2,500 rpm with constant torque thruout the speed range. Cooling jacket maintains low magnet temperature.

AGITATOR

Six blade flat turbine with a 2" diameter for speeds up to 2,500 rpm.

MOTOR DRIVE

Variable speed air motor for speeds up to 2,500 rpm. The motor requires an air supply of 40 psig and a flow rate of 16 scfm.

SUPPORT STAND

Steel floor stand complete with adjustable motor mount for easy belt adjustment. Included is an OSHA beltguard.

ACCESSORIES

Spare closure gasket. Removable thermowell, sample tube and cooling coil. Rupture discs (2) rated at 5,000 PSIG @ 650° F. Tachometer.

DESIGN OPTIONS

HEATING - Helical grooved body with shrink fitted 304 SS jacket. The jacket is rated for 100 PSIG at 650° F. Connections to the jacket are 1/4" N.P.T. An electric heating mantle is furnished with the jacket.

AGITATOR - Marine Propeller for mixing of liquid/liquid phase reactions vertically.

AGITATOR - Gaspersator for intimate mixing of the gas phase with the liquid phase using a shrouded six blade turbine.

MOTOR DRIVE - Variable speed AC/DC motor rated at 1/3 HP for a 115/1/60 power supply.

ACCESSORIES - Flush Valve, 1/2" diameter.
Removable wall baffles.
Gauge and Valve panel assembly.
Temperature control system.

SPECIFICATIONS AND DIMENSIONS

CAPACITIES

1000 ml	A = 3", B = 9⅜"
2000 ml	A = 3¾", B = 12¼"
1 gallon	A = 5", B = 12½"

DESIGN PRESSURE AND TEMPERATURE

5000 psig at 650°F.

MATERIALS OF CONSTRUCTION

316 S.S. for all process-contacting parts[1]

AGITATOR

Six blade flat turbine

HEATER

Flexible blanket heater for 120/1/60 or 240/1/60 power supply. Ratings are:

1000 ml	1.2 KW (120/1/60)
2000 ml	2.0 KW (120/1/60)
1 gallon	3.0 KW (240/1/60)

AGITATOR DRIVE

Variable speed air motor, 0-2500 rpm

STANDARD EQUIPMENT

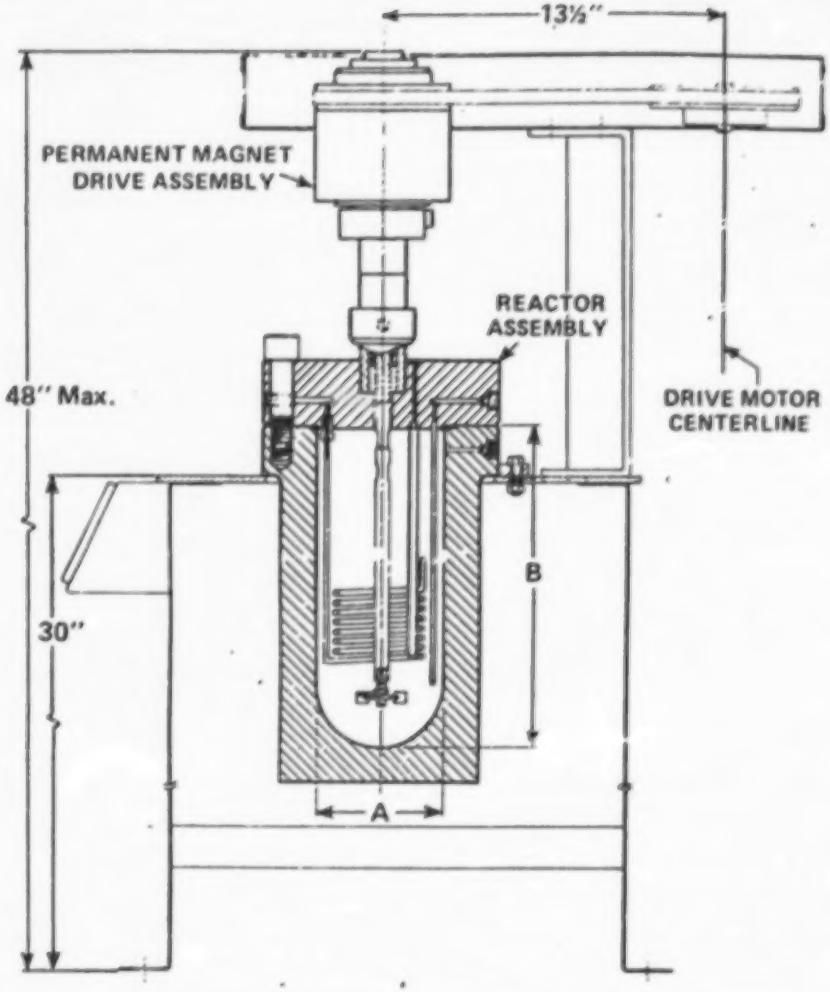
Sampling Tube, Cooling Coil, Rupture Discs (3), Thermowell, Spare Closure Gasket, Tachometer,

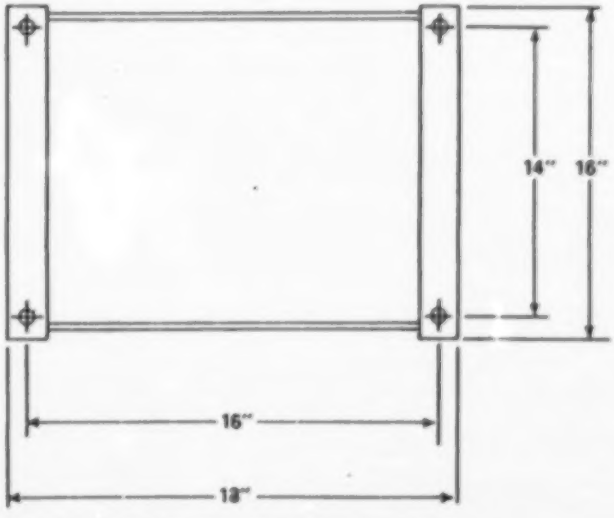
SYSTEM PROCESS CONNECTIONS

¼" Tubing, compression type

SHIPPING WEIGHT

1000 ml	185 lbs.
2000 ml	240 lbs.
1 gallon	390 lbs.

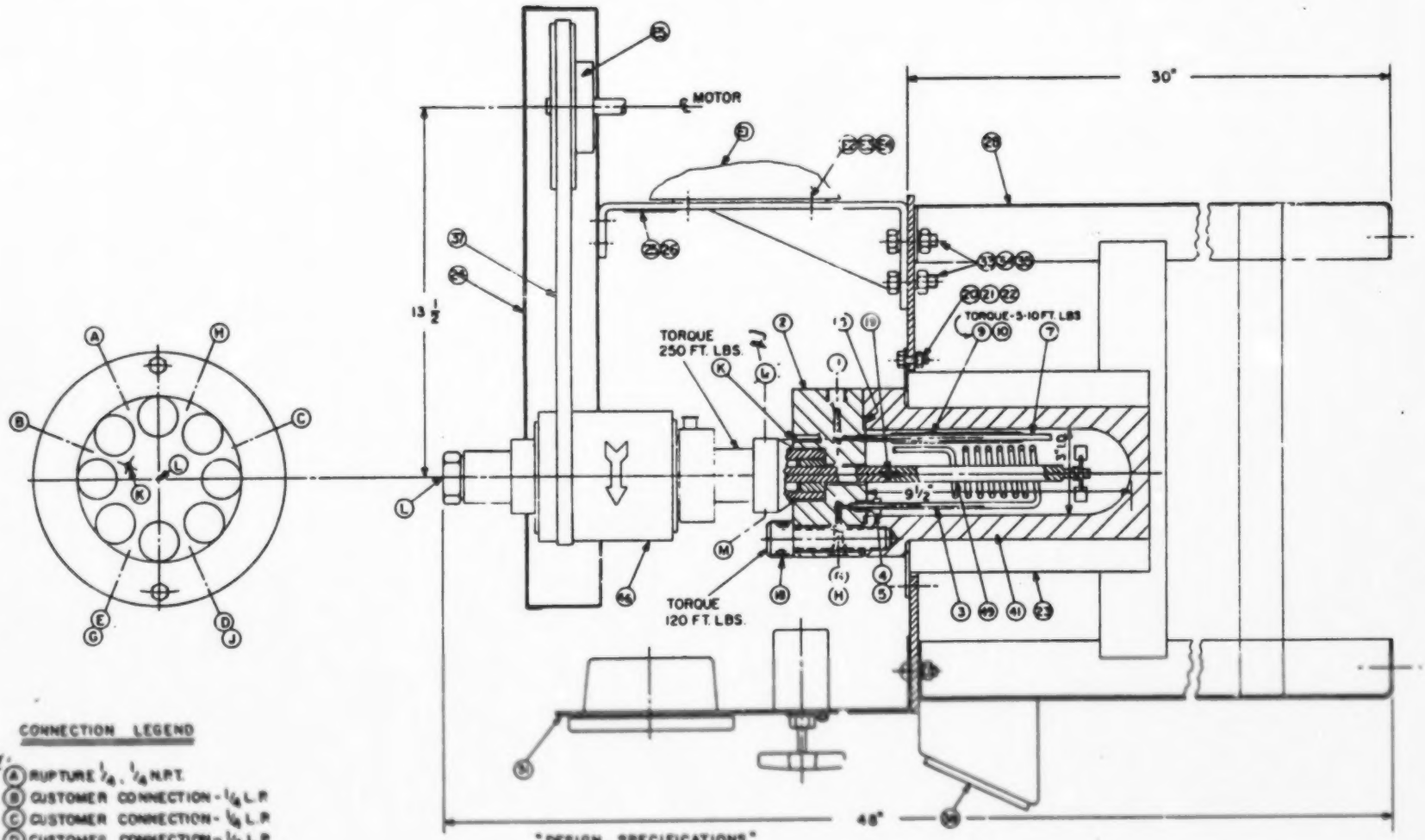




FLOOR MOUNTING DIMENSIONS

[1]For applications requiring higher alloy construction: Hastelloy B and C, Carpenter 20, Titanium, and Monel can be furnished. Consult your product specialist.

Note: For low speed, high viscosity agitation, PPI offers packed drive assemblies. Also available are Agitated Reactors for cap-



CONNECTION LEGEND

BODY:

- (A) RUPTURE 1/4, 1/4 N.P.T.
- (B) CUSTOMER CONNECTION - 1/4 L.P.
- (C) CUSTOMER CONNECTION - 1/4 L.P.
- (D) CUSTOMER CONNECTION - 1/4 L.P.
- (E) CUSTOMER CONNECTION - 1/4 L.P.

COVER:

- (G) COOLING COIL INLET - 1/4 N.P.T.
- (H) COOLING COIL OUTLET - 1/4 N.P.T.
- (J) SAMPLING TUBE - 1/8 L.P.
- (K) THERMOWELL - 9/32 DIA.

DRIVE

- (L) GAS INLET - 1/4 N.P.
- (M) COOLING INLE - 1/8 NPT
- (N) COOLING OUTLET - 1/8 NPT

"DESIGN SPECIFICATIONS"

CAPACITY		ONE LITER
DESIGN PRESSURE		5000 P.S.I.
DESIGN TEMPERATURE		650° F
HYDRO-TEST PRESSURE		8800 P.S.I.
DRIVE		MAGNETIC
AGITATION	OPTIONAL -	PROPELLER, TURBINE OR GASPERSATOR
HEATING		1.2 K.W., 120V., 60 HZ.

OPTION "B" & "BI"

JACKET DESIGN PRESSURE	100 P.S.I.
JACKET HYDRO-TEST PRESS.	200 P.S.I. @ 72° F.

PRESSURE PRODUCTS INDUSTRIES

ONE LITER REACTOR ASS'Y
MODEL (3MS) P.M.D. DRIVE

D-4910-0
SHEET 1 OF 4

DESIGN FEATURES

CLOSURE SEAL

The PPI closure design features ease of handling, reliability and low replacement cost. A specially designed spiral wound gasket is compressed between the body flange and cover. The gasket groove is designed so that the amount of compression on the gasket, from the bolt preload, is optimum. Preloading of the bolts brings the cover and body into metal to metal contact; therefore, over-compression of the gasket is eliminated.

Unlike metal seals, the soft spiral wound gasket conforms to irregularities in the seal surfaces, assuring a leak tight closure. The gasket can be reused many times and the actual operating life is a function of the care used in assembly and disassembly of the closure.

PROCESS CONNECTIONS

In PPI reactors, the process connections are located in the vessel body. Designing process connections in the body flange permits disassembly of the cover with minimum down time. The cover is removed without disturbing the pressure connections in the body flange. Not only does this save time it also eliminates excessive wear and possible damage to the tubing seats.

Each reactor is furnished with four process connections and a rupture assembly in the body flange. The cover is machined with cooling coil inlet and outlet connections plus a thermowell opening.

PROCESS AND SERVICE CONNECTIONS

BODY FLANGE	COVER
Rupture Assembly	Cooling Coil Inlet
Process Inlet	Cooling Coil Outlet
Process Outlet	Thermocouple/ Thermowell
Gas Inlet/Outlet	Sampling Tube

AGITATORS

The standard agitator is a flat multi-blade turbine. It is used for liquid solutions and also provides thorough agitation when used with baffles. Additionally, the Marine Propeller is available for liquid solutions requiring vertical mixing. If the gas phase is to be dispersed in the liquid phase, the "Gaspersator" turbine is recommended. It consists of a hollow shaft and a shrouded, flat-blade turbine arranged so that the gas phase is drawn down through the hollow shaft and dispersed from the tips of the turbine blades.

AGITATOR DRIVE SYSTEMS

A variety of motor drives are available and the eventual selection will depend upon the requirements of the agitator system, the economics of operation and the utilities available. The standard motor drive is an air motor and it is ideal for use in hazardous atmospheres where low cost, variable speed operation is required. Speed variations range from 0 to 2,500 rpm with an adequate air source. Also available is an AC/DC variable speed motor with the DC motor controlled by a remotely located control station. Speed variation is in the range of 10:1 and it is available with a Class 1, Group D explosion proof motor and a NEMA 1 control station.

HEATING

A flexible blanket heater with built-in insulation is provided with all electrically heated reactors. The wattage has been selected to minimize heat-up time and to obtain maximum operating life from the heating elements. Heaters are available for a 120/1/60 or 240/1/60 single phase power supply.

As an option, a combination heating-cooling jacket is offered. The jackets are supplied where high pressure steam or heat transfer systems are available. The jacket is welded to the reactor body. Inlet and outlet connections are provided. In addition, the electric blanket heaters can be attached to the jacket, providing the ultimate in rapid heat-up.

MOUNTING

A steel stand is provided to mount the reactor, drive, and accessories as a compact unit. An easily adjustable motor sheave permits convenient adjustment of belt drive tension. The rectangular stand design permits full access to the reactor body. OSHA beltguards are standard.

ACCESSORIES

- Flush Valve
- Removable Wall Baffles
- Gauge and Valve Panel Assembly
- Temperature Control